experiments in unbuffered, dilute alcohol solutions are shown in Table II. From the values $k_{II}^H/k_I^H = 182$, $k_{II}^D/k_I^D = 201$ and $k_I^H/k_I^D = 4.3$, the value of k_{II}^H/k_{II}^D is calculated to be 3.9.

Discussion

The deuterium isotope effect for the oxidation of ethanol by bromine in dilute, unbuffered solution may be compared directly with the previously determined tritium isotope effect.[2] Making the very rough approximation that the isotope effects arise from differences in the zero point energies associated with the stretching vibrations involving the isotopic hydrogen atoms in the normal and transition states of the reaction, and that the vibration frequencies for protium, deuterium and tritium are in the ratio $1:\sqrt{2}:\sqrt{3}$, it can be calculated that a value of k_H/k_D of 4.3 at 24.8° corresponds to a value of k_H/k_T of 7.5 at 37.5°. The latter value agrees, within the rather large uncertainties in both the experimental measurements and the oversimplified calculation, with the experimental value[2] of 6.7. This agreement between the competitively measured k_H/k_T and the kinetically measured k_H/k_D is in contrast to the case of the chromic acid oxidation of 2-propanol[8] in which reaction the processes studied by the competitive and non-competitive methods were not identical.

The observation that k_H/k_D for the oxidation of ethanol in 41% solution is identical with that in the 1 to 4% solutions removes any doubt of the validity of combining the isotope effect measurements in the dilute solutions with Farkas' kinetic results[3] in the concentrated solutions. The fact that the isotopic rate ratio, k_H/k_D, is as large as 4.3 requires the conclusion that a methylene C–H bond is broken in the rate-determining step of the reaction. This rate-determining step cannot, therefore, be the alcoholysis of bromine to ethyl hypobromite.

$$CH_3CH_2OH + Br_2 \longrightarrow CH_3CH_2OBr + HBr \quad (VIII)$$

Neither can equation VIII represent a rapid equilibrium preceding the rate-determining step, since such an equilibrium would require an inverse dependence of the reaction rate on HBr concentration, contrary to the findings of Farkas, *et al.*[3] It must be concluded, therefore, that ethyl hypobromite plays no role in the oxidation of ethanol, either as the precursor of acetaldehyde or as the oxidant of a second ethanol molecule. The lack of intervention by ethyl hypobromite in this oxidation is of particular interest since a number of oxidations of alcohols by inorganic oxidants in polar solutions have been shown or postulated to involve esters as intermediates.[9] The bromine oxidation, in contrast, appears to involve direct attack by molecular bromine, or a species with which it is in rapid equilibrium, at the C–H linkage of the alcohol, possibly abstracting hydrogen as hydride ion.[2,3] The similarity of the isotope effect ($k_H/k_D = 3.9$) in the acetaldehyde oxidation to that in the alcohol oxidation is in accord with the idea[3] that these reactions have similar mechanisms, the aldehyde reacting in the form of its hydrate or hemiacetal.

The occurrence of appreciable isotope effects in the oxidation of ethanol in solutions buffered at *p*H 5.5 and 10.2 indicate that under these conditions, also, the rate-determining steps involve rupture of a carbon–hydrogen bond. The reaction rates in solutions above *p*H 3, in contrast to those in unbuffered solutions at lower *p*H, are, however, markedly *p*H-dependent.[3,10] In the absence of a detailed analysis of the reaction kinetics, it is impossible to draw any conclusions with respect to possible intermediates in the oxidation under conditions of high *p*H.

Acknowledgment.—The author is indebted to Mrs. Judith Jero for technical assistance. He also expresses his appreciation to Dr. B. Perlmutter-Hayman for making available to him some unpublished results on the oxidation of ethanol solutions at high *p*H.

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[8] L. Kaplan, This Journal, **77**, 5469 (1955).

[9] L. S. Levitt and E. R. Malinowski, *ibid.*, **77**, 4517 (1955), suggest that such oxidations *always* go through the intermediate stage of ester formation.

[10] B. Perlmutter-Hayman, private communication.

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Effect of Temperature, Pressure, Acidity and Solvent on an Aquo Ion Exchange Reaction

BY H. R. HUNT AND H. TAUBE

RECEIVED DECEMBER 11, 1957

$\Delta V^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ for the exchange of water between $(NH_3)_5CoOH_2^{+++}$ and solvent have been measured as $+1.2 \pm 0.2$ ml., $+6.7 \pm 1$ e.u. and 26.6 ± 0.3 kcal. mole^{-1}. The values of $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ observed, and the added observation that $\Delta V^{\ddagger}$ is independent of pressure, appear to rule out an extreme or compact S_N2 mechanism. The observations require that the Co(III)–OH_2 bond in the activated complex be stretched to a critical value; however, they provide no basis for deciding whether a true intermediate is formed on decomposition of the activated complex or whether some use is made of the entering water molecule in the activation process. The rate of water exchange is almost independent of the concentration of water when CH_3OH is principal component of the solvent mixture. The exchange rate for $(NH_3)_5CoOH^{++}$ is much less (by a factor of at least 40) than it is for $(NH_3)_5CoOH_2^{+++}$.

Many substitution reactions of metal complex ions in water proceed by intermediate aquation. The exchange of water with an aquo ion, therefore, has special significance to the problem of the mechanism of the substitution reactions.[1] Because rate law methods fail to define the composition of the activated complex with respect to solvent, the

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[1] J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).

problem of mechanism for solvent–solvated ion interactions is a particularly difficult one. The mechanism is undefined even with respect to an important feature such as this: does the slow step involve merely stretching the cation–OH_2 bond, or is the incoming solvent molecule required to make a bond as the one being replaced leaves?

In this paper we describe attempts to define the nature of the activated complex for the reaction

$$(NH_3)_5CoOH_2^{+++} + H_2O^* = (NH_3)_5CoO^*H_2^{+++} + H_2O$$

(The radical $(NH_3)_5Co$ will hereinafter be represented by R.) The reaction is well suited for the study by virtue of its tractability, simplicity and its relevance to a great deal of other work on substitution reactions of complex ions.

Earlier work[2] showed that exchange data of high quality readily can be obtained. Specific conclusions as to kinetics from this earlier work are: the reaction is strictly first order in ROH_2^{+++}, it is independent of acid over a considerable range (0.008 to 0.07) and is unaffected by at least moderate changes in ionic strength.

The work now being reported augments this information by the results of a study of the variation of the rate of exchange with temperature and with pressure, of the kinetics when CH_3OH is principal component of the solvent mixture, of the influence of the acidity when it is low enough so that a substantial fraction of the ROH_2^{+++} is present as ROH^{++}. The rationale of the temperature and pressure studies is that they lead to values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$, quantities which help to define the nature of the activated complex. The other two studies are not so directly relevant to the central point of the paper, but they do add interesting information on the chemical behavior of the system.

Experimental

Reagents.—The salt $ROH_2(ClO_4)_3$ was enriched in O^{18} by dissolving 10 g. of it in 100 ml. of O^{18}-enriched water made 0.005 *M* in $HClO_4$. The solution was kept at 50° for 24 hr., then cooled in an ice-salt bath to precipitate the enriched salt, which was removed, washed and dried. Ten such batches were prepared and combined. To ensure uniformity of isotopic composition, the combined salt was dissolved in and precipitated from ordinary water. This operation was carried out by dissolving rapidly at 50°, adding perchloric acid to incipient precipitation, and then cooling the solution in an ice-bath. The precipitate was filtered, washed with cold water and dried.

$ROH_2(ClO_4)_3$ was prepared as described earlier.[2]

CH_3OH was treated to remove water, using the method of Lund and Bjerrum.[3]

Water, whether enriched or of normal isotopic composition, was purified by redistillation from alkaline $KMnO_4$.

All reagents were of AR quality.

Procedures.—Sampling to obtain the isotopic composition of the ion ROH_2^{+++} was done by the method of Posey,[4] which involves precipitation of ROH_2Br_3, rather than by the method originally proposed by Rutenberg.[2] Removal of the bound water and determination of the isotopic composition followed methods described in the associated references.

Of the experimental methods specific to each part of this study, only those dealing with the effect of pressure on rate require special mention. The pressure apparatus is of the type described by Jamieson and Lawson[5] and was made available through the courtesy of Professor A. W. Lawson of the Institute for the Study of Metals, University of Chicago. The working bomb contained a cylindrical cavity *ca.* 1³/₁₆″ diameter by 2³/₄″ long. Pressure was measured by means of a manganin coil resistance gauge. The pressure was controlled to ±1%. The temperature was measured at two points near the cell in the silicone oil which was the working fluid. An external oil-bath was used to thermostat the cell within ±0.1°. The cell was a Teflon cylinder fitted with a movable plug (which was tapped with a Teflon screw for release of trapped air bubbles) and was of 15-ml. capacity.

A temperature rise takes place during the pumping up process. This rise is reproducible, if the pumping procedure is made reproducible. This being so, it does not introduce a serious complication. For a given pressure, individual samples were run for various lengths of time, the minimum time being great enough to ensure that the heat developed in pumping had been dissipated.

(A) **Temperature Dependence of the Exchange Rate.**—The data on the rate of exchange as a function of temperature are shown in Table I.

TABLE I

EFFECT OF TEMPERATURE ON THE RATE OF EXCHANGE

(ROH_2^{+++} = 0.100 *M*; $HClO_4$, 0.006 to 0.010 *M*)

Temp., °C.	k_1, hr.$^{-1}$
25.1	0.0212
35.0	.0930
44.7	.335

The data yield for the parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the equation[6]

$$k_1 = \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

26.6 ± 0.3 kcal. mole^{-1} and 6.7 ± 1 cal. deg.$^{-1}$ mole^{-1}, respectively. The earlier value obtained by Rutenberg at 27.0° agrees very well with the present data.

(B) **Effect of Pressure on Rate on Exchange.**—In one experiment at 25°, a pressure of 2080 atm. was used. The ratio of specific rates for this pressure compared to atmospheric was observed as 0.903. In a second experiment (this at 30.3°), the pressure was raised to 7000 atm. The specific rate ratio for 7000 atm. compared to 1 atm. was observed as 0.740. Using the equation[6]

$$\Delta V^{\ddagger} = \frac{RT \ln k_2/k_1}{P_1 - P_2}$$

$\Delta V^{\ddagger}$ from the data cited for the first experiment is 1.2 ± 0.2 ml. mole^{-1}, and that for the experiment at higher pressure is 1.1 ± 0.2 ml. In addition to establishing the value of $\Delta V^{\ddagger}$, the data show that $\Delta V^{\ddagger}$ is substantially independent of pressure.

(C) **The Rate of Exchange as a Function of Acidity.**—The results of the experiments we have done on solutions of ROH_2^{+++} to which progressively greater amounts of NaOH have been added are reported in Table II.

TABLE II

EXCHANGE OF H_2O BETWEEN ROH_2^{+++} AND SOLVENT AS A FUNCTION OF ACIDITY

Temp. = 25.25 ± 0.05°; $ROH_2(ClO_4)_3$ = 0.025 *M*

$\frac{(OH^-)_0}{(RH_2O^{+++})_0}$	k, hr.$^{-1}$
0.35	0.0138
0.70	.00645
1.05	.0005

In the third experiment, reported in Table II, substantially all of the aquo ion has been converted to ROH^{++}. The value of *k* measured in this experiment is an upper limit for the rate at which ROH^{++} exchanges oxygen with water. The value given is only approximate because exchange had proceeded only 2% to completion by the time the last sample was taken. Since irreversible changes accompany the exchange, it is doubtful whether a much more accurate value can be obtained. The specific rate for the

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[2] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 825 (1952).

[3] H. Lund and J. Bjerrum, *Ber.*, **64B**, 270 (1931).

[4] F. A. Posey and H. Taube, THIS JOURNAL, **79**, 255 (1957).

[5] J. C. Jamieson and A. W. Lawson, "Ninth Annual Report to ONR on High Pressure Research," (ONR Contract No. N-6080-02020) NR 017 035 p. 2 (1956).

[6] S. Glasstone, R. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

exchange of ROH_2^{++} with H_2O at 25.25° is 0.0217 hr. If it is assumed that in experiments 1 and 2 of Table II, 35 and 70%, respectively, of the aquo ion is inert to exchange, the calculated specific rates for these experiments are 0.0141 and 0.0065 hr.$^{-1}$. The comparison with the experimental value leaves no room for an appreciable contribution to the exchange by an activated complex of composition of $(NH_3)_5CoOH^{++}$. Thus the figure in experiment 3 is a generous upper limit for the specific rate coefficient for the term $((NH_3)_5CoOH^{++})$. The value of 0.0005 may actually correspond to the coefficient for the rate term $(ROH^{++})(OH^-)$.

(D) **Rate of Exchange in Methanol-Water Mixtures.**—The specific rates measured for the exchange of ROH_2^{+++} with H_2O in CH_3OH-H_2O mixtures are reported in Table III.

TABLE III

EXCHANGE OF H_2O BETWEEN ROH_2^{+++} AND SOLVENT IN WATER-METHANOL SOLUTIONS

$(ROH_2^{+++}) = 0.005$ *M*; $(HClO_4) = 0.01$ *M*; temp. = 25.2°)

Exp.	H_2O, mole l.$^{-1}$	*k*, hr.$^{-1}$
3.01	2.22	0.0065
3.02	4.44	.0076
3.03	6.66	.0085

Each value of *k* is based on three samples at different times. The data showed a small but significant deviation from simple behavior. In each experiment, the second point in a plot of $\log(N_t - N_\infty)$ *vs.* time was slightly higher than the line through the remaining two, so that the curves are slightly concave downward.

This behavior is what would be expected if net substitution of CH_3OH in the aquo ion takes place, with exchange and alcoholate formation competing for a common intermediate. A number of experiments were done to check this important point, but the results, while indicating some alcoholate formation, are inclusive as to the extent of this reaction.

No change in the two absorption bands of ROH_2^{+++} in the visible is observed over a long period of time when ROH_2^{+++} is dissolved in a CH_3OH-H_2O mixture, of the composition used in exp. 3.01. There is a gradual increase in absorption in the near ultraviolet, but no proof has been given for the cause of this change.

Analysis for CH_3OH was made in the H_2O collected from the ROH_2Br_3 for isotopic analysis (any alcoholate present here would presumably have yielded CH_3OH during heating). The results of the analysis by the chromotropic method[7] are shown in Table IV.

TABLE IV

ANALYSIS FOR CH_3OH IN H_2O OBTAINED FROM ROH_2Br_3 SAMPLES AS USED FOR DATA OF TABLE III

Sample no.	Time of sampling, hr.	Mole % CH_3OH Exp. 301	302	303
1	2	0.05	..	0.07
2	26	.35	0.23	.21
3	48	.35	0.27	.21

The data do show that there is some net substitution of H_2O by CH_3OH, which reaches equilibrium before 26 hr. has elapsed and which decreases in extent as water content increases. The amount of substitution as shown by the figures in Table IV is, however, too small to account for the effect we have observed.

It is likely that only a small fraction of the methanolate formed survives the treatment with HBr which precedes precipitation of the compound (this view is supported by the observation cited by Brown, Ingold and Nyholm[8] that Cl^- rapidly replaces CH_3OH when HCl is added to a solution containing a methanolate substituted complex). In an effort to reduce the intensity of our ordinary drying procedure, some samples were dried by washing with C_2H_5OH rather than following the usual method. Somewhat greater CH_3OH contents were found for these samples than for those reported in Table IV, but the results were erratic, and the methanol content did not reach 1 mole %.

Discussion

It should be stressed at the outset that with regard to pressure effects, solvent exchange reactions occupy a unique position. In most other reactions, large changes in charge separation occur in transforming the reactants to the activated complex, and the values of $\Delta V^{\ddagger}$ are mainly dependent on the consequent changes in electrostriction of the solvent.[9] In the reaction under present study, H_2O is being separated from the cation, leaving the center of positive charge largely undisturbed. The volume effect on solvation of water by water is accurately known, and it may be assumed that the electrostriction effects through the residue $(NH_3)_5Co^{+++}$ are not much different in the activated complex and in the reactants. Therefore, the values of $\Delta V^{\ddagger}$ observed are ascribed largely to the seat of the reaction. On this basis, a self-consistent discussion of the pressure effects is possible which, moreover, is consistent with other evidence to be adduced.

The process of activation for the exchange reaction under study, which is suggested by the pressure data, is one in which the $Co(III)-OH_2$ bond stretches to a definite critical distance. On this basis, a positive value for $\Delta V^{\ddagger}$ would be expected (as is observed) but not as large as would be the case if the activated complex were to have the properties of the products of an S_N1 process

$$ROH_2^{+++} \longrightarrow R^{+++} + H_2O \qquad (1)$$

For the reaction represented in equation 1, the value of $\Delta V^{\ddagger}$ would be expected to be very nearly equal to the difference in molal volumes of water when it is bound in the first coördination sphere of Co(III) and when it is part of the liquid. Biltz[10] estimates 14.4 ml. as the molal volume of water in the ion ROH_2^{+++} (not all estimates agree with this one; Birk[11] estimates 17.0 ml. for the same quantity). Thus for an activated complex resembling the products of reaction I, $\Delta V^{\ddagger}$ would be measured as 3.6 ml. (accepting Biltz' estimate of the molal volume of coördination water and assuming that the residue $Co(NH_3)_5$ occupies equal volumes as reactant and product).

The observation that $\Delta V^{\ddagger}$ is independent of pressure is consistent with the model advanced for the activated complex. The requirement that there be a minimum critical value for the $Co(III)-OH_2$ separation accommodates the observation that $\Delta V^{\ddagger}$ is constant up to pressures as large as 7000 atm.

The experimental results on the pressure effect appear to have some force in suggesting the features of the activated complex which have been described; they have even greater force in eliminating a model in which the water molecule leaving is stretched only slightly from its equilibrium position, and the water molecule entering occupies an equivalent position in the activated complex. For

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[7] R. N. Boos, *Anal. Chem.*, **20**, 946 (1948).

[8] D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

[9] C. T. Burris and K. J. Laidler, *Trans. Faraday Soc.*, **51**, 1497 (1955).

[10] W. Biltz, *Z. anorg. Chem.*, **164**, 245 (1927).

[11] E. Birk, *ibid.*, **158**, 111 (1926).

a compact S_N2 mechanism of this kind

$$ROH_2^{+++} + H_2O \rightleftarrows [R(OH_2)_2^{+++}]^{\ddagger} \quad (2)$$

$\Delta V^{\ddagger}$ should be negative, in the limit by 3.6 ml., but actually by less than this because any stretching of the Co(III)–OH_2 bond would give rise to a positive contribution to $\Delta V^{\ddagger}$. The argument based on the constancy of $\Delta V^{\ddagger}$ is even more powerful in eliminating process (2). Since at 7000 atm., the molal volume of water has decreased to 15.1 ml.[12] and since the first coördination sphere for a tripositive cation is much less compressible than is bulk water, $\Delta V^{\ddagger}$ should be strongly pressure dependent for any process that involves equilibrium between solvent water and coördination water. In fact, this effect, which arises because of the large compressibility of liquid water, would be so great that $\Delta V^{\ddagger}$ at 7000 atm. could even change sign if the activation process were of the type represented in equation 2.

Arguments similar to those advanced for the significance of $\Delta V^{\ddagger}$ can be made for the significance of $\Delta S^{\ddagger}$. Reaction proceeding by an extreme S_N2 path would be expected to give rise to value of $\Delta S^{\ddagger}$ of about −7.3 e.u. (the difference[13] in entropy between water bond in the first coördination sphere and water as part of the solvent). The positive value of $\Delta S^{\ddagger}$ observed suggests that the water molecule gains freedom of movement in the activation process. If the Co(III)–OH_2 bond is stretched sufficiently in the activated complex so that motion perpendicular to this bond becomes possible and rotation about this bond can take place much as for in a molecule which is part of the liquid, a value of $\Delta S^{\ddagger}$ of about +7 e.u. would be expected—slightly less because the motion along the Co(III)–OH_2 bond does not contribute to $\Delta S^{\ddagger}$. The value of $\Delta S^{\ddagger} = 6.7$ observed is in satisfactory agreement with this model.

It is clear that although the experiments seem to eliminate an extreme S_N2 mechanism, they do not make a sharp distinction between S_N1 and S_N2 processes. Thus all of the mechanisms described in the following, ranging from an extreme S_N1 type to one which possesses features of an S_N2 process, are consistent with the data: (a) a true intermediate ($Co(NH_3)_5^{+++}$ aq.), which is at equilibrium with respect to internal strain and to solvation, is formed; (b) the new bond is made immediately after the original water molecule has exceeded the critical distance from Co(III), but before the residue has had time to adopt an equilibrium configuration; (c) the entering water molecule makes a weak bond in the activated complex (but the interaction must be so weak that the entropy of the entering water molecule is not much different from what it is in the liquid).

Other evidence argues against the extreme S_N1 mechanism, at least as applicable to all substitution reactions involving H_2O. Experiments on the fractionation[4] of oxygen isotopes in the aquation of complexes of the type RX^{++} induced by metal ions, suggest that only in the case of Hg^{++} reacting with the complexes is an intermediate formed which reaches equilibrium with respect to solvation. It seems likely, therefore, that in the absence of an interaction as effective as that of Hg^{++} in weakening the Co(III)–ligand bond, some use is made of the incoming group in the activated complex. In addition, it can be mentioned that there is some difficulty in reconciling the data[14] on the substitution of H_2O in ROH_2^{+++} by $SO_4^{=}$ with the present data, on the assumption that all the substitutions take place entirely by an S_N1 mechanism. The activation energy for the substitution of H_2O by $SO_4^{=}$ is about 4 kcal. less than for the water exchange. It is difficult to see how the reaction of $SO_4^{=}$ with an intermediate such as $Co(NH_3)_5^{+++}$ can be as much as 4 kcal. less than the reaction of H_2O with the same intermediate. It seems more likely that use is made of the $SO_4^{=}$ in weakening the Co(III)–OH_2 bond in the activated complex. The outer sphere association of $SO_4^{=}$ with $Co(NH_3)_5^{+++}$ is unlikely to be accompanied by such a large heat effect—thus ΔH for the association of $Co(NH_3)_5OH_2^{+++}$ with $SO_4^{=}$ is about zero.[15] However, as in the case of water exchange, if the entering group makes a bond as the water being replaced is removed, its distance from the Co(III) in the activated complex is large; this conclusion is indicated because the activated complex has about the entropy of the outer sphere complex $ROH_2^{+++}\cdot SO_4^{=}$.

The conclusion that in $SO_4^{=}$–H_2O exchange both species interact with Co^{+++} in the activated complex does not require that a precisely similar mechanism operates for H_2O–H_2O exchange. The much stronger solvation of a negative ion compared to water may have direct consequences in details of the substitution reaction. When $SO_4^{=}$ moves away from Co(III), a water molecule from the hydration shell of the anion may be in better position to take the place of the anion than is the case when OH_2 moves away from Co(III) and another molecule of H_2O takes its place.

The results of the experiments in CH_3OH suggest that in this medium the reaction takes place in large part without making use of water in the activated complex. The basis for this conclusion is the observation that the rate of exchange is almost independent of the concentration of water over the three-fold range studied. The question of whether a solvent molecule is needed to form a bond as the group being replaced leaves is not further illuminated by these experiments. Thus, the activation in CH_3OH may consist in a Co(III)–CH_3OH complex being formed by an S_N2 process, with rapid replacement in turn of CH_3OH by H_2O. In fact, when the specific rates in Table III are plotted against the mole fraction of H_2O, a straight line is obtained which has an intercept of 0.0054 hr.$^{-1}$ at zero water (pure CH_3OH) and which extrapolates nearly to the observed specific rate in pure H_2O.

The most convincing evidence on the question of detailed mechanism may come out of further work on the apparent competition between exchange with water and substitution by solvent in methanol. The data thus far are inconclusive on this question.

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(12) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **48**, 309 (1912).

(13) W. M. Latimer and W. J. Jolly, THIS JOURNAL, **75**, 1548 (1953).

(14) H. Taube and F. A. Posey, *ibid.*, **75**, 1463 (1953).

(15) F. A. Posey and H. Taube, *ibid.*, **78**, 15 (1956).

The point that a change in solvent from H_2O to CH_3OH causes a considerable change (four-fold decrease) in rate, but yet no effect on the rate is admitted arising out of altering the solvent water by compressing it to a molar volume of 15 ml., requires some comment. It can be argued that because the solvent in the neighborhood of an ion of high charge is already highly compressed, no large change in the solvent in this region is effected by increasing the pressure. Change from one solvent to another does, however, alter the immediate environment of the cation. Thus, the change in rate caused by changing solvent does not appear to be incompatible with the assumption that the pure solvent effect caused by increase in pressure does not give rise to a large change in rate.

In a number of substitution reactions, it has been observed that the rate of aquation or hydrolysis increases as the acidity decreases. The marked decline in rate of exchange for ROH_2^{+++} as alkali is added, therefore, seems surprising at first sight. Closer examination of the system shows that the result is not inconsistent with the observations on other complexes. A specific rate ratio of 10^3 to 10^5 has been estimated[16] for the replacement of X in $(NH_3)_4CoNH_2X^+$ as compared to $(NH_3)_5CoX^{++}$, and a similar ratio can be assumed for $(NH_3)_4CoNH_2OH_2^{++}$ as compared to $(NH_3)_5CoOH_2^{+++}$. However, in a solution in which $(NH_3)_5CoOH^{++}$ is the dominant form, only a small fraction is present as $(NH_3)_4CoNH_2OH_2^{++}$, this fraction being determined by the relative acidities of coördinated H_2O as compared to coördinated NH_3. The fraction in question may be as small as 10^{-7}; therefore, the specific rate of exchange when $(NH_3)_5CoOH^{++}$ is dominant is expected to be 10^{-4} to 10^{-2} times that for $(NH_3)_5CoOH_2^{+++}$. Experimentally, it is found that this ratio is no greater than 2×10^{-2}.

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[16] R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956).

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Determination of the Formulas of Aqueous Ruthenium(III) Species by Means of Ion-exchange Resin: Ru^{+3}, $RuCl^{+2}$ and $RuCl_2^+$

BY HOWARD H. CADY AND ROBERT E. CONNICK

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The formulas of some aqueous ruthenium(III) species have been determined by a method which utilizes the properties of ion-exchange resins. The method is applicable when equilibria between the species of interest and other species of significant concentration are established slowly, and when the species of interest can be isolated in solution, as for example certain complex ions. In one experiment the charge per metal atom is found from the equivalents of charge exchanged with an ion-exchange resin per gram atom of the metal. In a second experiment the total charge per species is determined from the concentration dependence of the ion-exchange equilibrium of the unknown species with an ion of known charge. The total charge divided by the charge per atom gives the degree of polymerization of the species. The stoichiometric formula can be inferred when a single anion is involved in complexing. The method has been employed to establish the formulas of the species Ru^{+3} and $RuCl^{+2}$. A species shown to have a total charge of +1 is probably $RuCl_2^+$. The separation of the ruthenium species was accomplished by "pushing" with cerous ion a dilute mixture of species on an ion-exchange column, with the result that nearly pure bands of the individual species were obtained at high concentration.

Little is known regarding the formulas of aqueous ruthenium species in the +2, +3 and +4 oxidation states.[1,2] Preparations customarily yield mixtures of species corresponding to different complexes and varying degrees of polymerization, as well as mixtures of oxidation states. Because equilibria between the species are established slowly it is impractical in most cases to use equilibrium measurements to establish the formulas. Colligative determinations are not employed because of the difficulty of preparing pure species.

It was desirable to have as general a method as possible for the identification of ruthenium species. One has been developed which makes use of ion-exchange measurements.[3] Two experiments are performed. First, the charge on the species per ruthenium atom, a, is found. Second, the total charge per species, b, is measured. The ratio b/a equals the number of ruthenium atoms per species. If the oxidation number of the ruthenium is known, the number of negative charges contributed to the species by anions can be inferred. If only one anion is involved, the complete formula of the species is determined. The method has been used to identify Ru^{+3} and $RuCl^{+2}$. A chloride complex of the +3 oxidation state with b equal to +1 was detected and it is presumed to be $RuCl_2^+$.

Determination of Charge per Metal Atom.—The method is based on the fixed exchange capacity of the resin, measured in equivalents of charge. The charge per metal atom, a, is equal

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[1] (a) The older literature is summarized in Gmelin's Handbuch der anorganischen Chemie, System No. 63, 8th Edition, Verlag Chemie, Berlin, 1938; (b) more recently D. D. Deford has critically reviewed the literature in his doctoral thesis at the University of Kansas (May, 1948), which has been reproduced by the United States Atomic Energy Commission as an unclassified document, NP-1104, Nov. 30, 1949.

[2] Recent work is to be found in: (a) P. Wehner and J. C. Hindman, THIS JOURNAL, **72**, 3911 (1950); (b) P. Wehner and J. C. Hindman, *J. Phys. Chem.*, **56**, 10 (1952); (c) L. W. Niedrach and A. D. Tevebaugh, THIS JOURNAL, **73**, 2835 (1951); (d) J. R. Backhouse and F. P. Dwyer, *Proc. Roy. Soc. New South Wales*, **83**, 138 (1949); **83**, 146 (1949).

[3] R. E. Connick and H. H. Cady, THIS JOURNAL, **79**, 4242 (1957).